

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-292568

(43)Date of publication of application : 26.10.1999

(51)Int.Cl.

C03C 17/02

B60J 1/00

G02B 1/11

G02B 5/02

(21)Application number : 10-345273

(71)Applicant : NIPPON SHEET GLASS CO LTD

(22)Date of filing : 04.12.1998

(72)Inventor : TAKAHASHI YASUSHI
OKAMOTO HIDEKI

(30)Priority

Priority number : 09338363 Priority date : 09.12.1997 Priority country : JP

(54) ANTIREFLECTION GLASS SHEET, ITS PRODUCTION AND COATING COMPOSITION FOR ANTIREFLECTION FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain small reflectance for visible light of a large incident angle and to improve visibility by coating the surface of a glass substrate with a film which has specified thickness and consists of chain silica fine particles and silica, and forming a rough surface of the film.

SOLUTION: At least one surface of a glass substrate is coated with a film of 110 to 250 nm thickness comprising chain silica fine particles and silica by 5 to 30 wt.% of the chain silica, and the surface of the film is roughened. The obtd. film has voids in chain silica particles adjacent to each other in the film, and the film has 1.25 to 1.40 refractive index. The film surface has 5 to 50 nm numerical average roughness (Ra) with 10 to 300 nm average period (Sm) of roughness. A preferable film compsn. is obtd. by compounding 100 pts.wt. of a silicon compd., 100 to 800 pts.wt. of chain silica fine particles, 4 to 150 pts.wt. of water, 0.00001 to 5 pts.wt. of an acid catalyst, 0.001 to 10 pts.wt. of a dispersion assistant and 500 to 10000 pts.wt. of a solvent to prepare the coating liquid.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] An acid-resisting glass plate, especially the light reflection factor of this invention are small, and it relates to the glass plate suitable for an automobile aperture, the method of manufacturing it, and the coat constituent for antireflection films.

[0002]

[Description of the Prior Art] Conventionally, the light reflects on the front face of the glass article of a glass plate and others, and in order for fluoroscopy nature and light transmittance to fall or to prevent becoming dazzling, performing acid-resisting processing to the front face of a glass article is performed.

[0003] For example, the low refractive-index antireflection film which applied to the base material the spreading liquid which made the solvent contain the silica sol which has the particle diameter of 5-30nm, and the hydrolyzate of alkoxysilane, and was hardened is known (JP,8-122501,A).

[0004] In the front window glass of an automobile, in order that the light from an instrument panel (instrument panel) in the car, a dashboard, etc. may reflect on the front face of front window glass and the reflected image of an instrument panel and a dashboard may go into an operator's field of view, there is a problem to which the visibility ahead of an operator falls. It emits from an instrument panel and a dashboard, and in order that the light which carried out [light] incidence and was reflected by the quite big incident angle to front window glass may go into an operator's eyes, in order to improve this visibility, it is necessary to reduce the reflection factor of the front window glass in a high incident angle (for example, 60 degrees). And the above-mentioned low refractive-index antireflection film is not enough for reduction of the reflection factor in a high incident angle, and it cannot be said that visibility is high enough.

[0005]

[Problem(s) to be Solved by the Invention] The reflection factor of this invention of the light in a high incident angle is small, and it aims at offering the glass plate suitable for the automobile aperture whose visibility improved.

[0006]

[Means for Solving the Problem] This invention is a light acid-resisting glass plate with which it consists of 5 - 30% of the weight of a silica to weight of a chain-like silica particle and its chain-like silica particle, a film which has thickness of 110-250nm is covered by at least one side on a front face of a glass substrate, and irregularity is formed in the film front face.

[0007] Moreover, this invention is a light acid-resisting glass plate with a small reflection factor in a high incident angle with which it consists of a chain-like silica particle and a silica, and a film which has thickness of 110-250nm is covered by at least one side on a front face of a glass substrate, an opening is generated, the film has a refractive index of 1.25-1.40 between chain-like silica particles which adjoin mutually within a film, and irregularity is formed in the film front face.

[0008] In this invention, a film for acid resisting which consists of a chain-like silica particle and a silica on the surface of a glass substrate is covered, and irregularity by the shape of surface type of a chain-like

silica particle which projects and exists there is formed in a front face of the film.

[0009] The above-mentioned film consists of a small amount of silica which does not have 5 - 30% of the weight of a particle configuration to weight of a chain-like silica particle preferably than a chain-like silica particle and it, and a silica is useful to adhesion of chain-like silica particles, and adhesion with a silica particle and a glass substrate front face as a binder.

[0010] Although a thing of a configuration straightly extended in the shape of a straight line as the above-mentioned chain-like silica particle may be used, a thing of a configuration which curved in [it is two-dimensional more desirable and] three dimensions is used most preferably. By using a silica particle of a chain-like configuration, a gap (gap) of 5-20nm width of face is formed among adjoining chain-like particles in a film. This gap has a far big whole product as compared with a gap formed when using a spherical silica particle of this weight instead of a chain-like silica particle. And since there is little amount of silica used as a binder on which chain-like particles are pasted up, there is nothing into which all the above-mentioned gaps are filled up with a silica binder and that is done, and most gaps remain as an opening (space) which air or a gas occupies. By existence of the opening, a value of a refractive index as the whole film becomes small, and is set to 1.25-1.40 from a refractive index (about 1.45) of a silica. Although a value of a refractive index of an antireflection film with which a reflection factor serves as zero theoretically is a square root value of a refractive index (1.50) of a glass substrate, 1.225 [i.e.,], it can bring a refractive index of an antireflection film of this invention close to this value.

[0011] There are not much too few amounts of a silica as a binder in a film, for example, to weight of a chain-like silica particle, in being less than 5 % of the weight, it becomes inadequate pasting [of a chain-like silica particle] up and a membranous mechanical strength falls. Since a silica fills a gap between chain-like silica particles and an opening does not remain in reverse's having not much too many amounts of a silica, for example, exceeding 30 % of the weight to weight of a chain-like silica particle, it becomes impossible to make a membranous refractive index small, and it becomes impossible moreover, to make a reflection factor low. Volume of the above-mentioned opening is calculated from a difference of a refractive index of the surveyed above-mentioned film, and a refractive index (about 1.45) of a film which made [many] the amount of silicas to a chain-like silica particle, and filled a gap of chain-like silica particles with a silica, and is presumed to be 50 - 80% of the volume of the whole film.

[0012] Since very small irregularity by convex front face of a chain-like silica particle is mainly formed in a film front face, the reflected light is diffused, reflected [a reflected image] is prevented, and, moreover, resolution of a fluoroscopy image does not fall. And if there are not much too many amounts of a silica as a binder in a film, the whole chain-like silica particle will sink in the bottom of a silica. Arithmetic mean granularity on a front face of a film mentioned later (R_a) is set to less than 5nm, and an average gap (S_m) of irregularity on a front face of a film becomes easy to exceed 300nm, and it becomes impossible therefore, to prevent reflected [a reflected image] effectively. Therefore, in order to make a membranous refractive index low and to make the above-mentioned irregularity form in a film front face moreover, without reducing a membranous mechanical strength, as for an amount of a silica in a film, it is desirable to consider as 5 - 30 % of the weight to weight of a chain-like silica particle, and it is 10 - 20 % of the weight more preferably.

[0013] As for magnitude of the above-mentioned chain-like silica particle, it is desirable to have an average diameter of 10-20nm and an average length of 60-200nm. With an average diameter, each diameter of 100 taken-out samples is measured with an electron microscope here. It is the value which attached a wait proportional to the volume to the measured value, and asked for an average. Average length is the value which measured each length (length which met the deflection when curving) of 100 taken-out samples with an electron microscope, attached a wait proportional to the volume to the measured value, and asked for an average similarly.

[0014] Less than 10nm or average length in less than 60nm [an average diameter of a chain-like silica particle] (1) The whole gap product between adjoining particles becomes small, therefore the whole opening product becomes small. Since it becomes impossible for arithmetic mean granularity on a front face of a film which it becomes impossible to make a value of a refractive index as a film small, and is

(2) Obtained (Ra) to form sufficient effective irregularity to be set to less than 5nm and prevent reflected [a reflected image], it is not desirable. Moreover, if an average diameter exceeds 20nm or average length exceeds 200nm, since arithmetic mean granularity on a front face of a film (Ra) becomes larger than 50nm, resolution of a fluoroscopy image will tend to fall, Hayes will become [it will become, or] being easy to generate and visibility will fall, it is not desirable.

[0015] Here, arithmetic mean granularity (Ra) and a concavo-convex average gap (Sm) can measure JIS B 0601 (1994) defined by two dimensions by method extended to three dimensions using an atomic force microscope (AFM) (a product made from SEIKO Electronic industry, a scan mold probe microscope "SPI3700", a cantilever; product made from silicon "SI-DF20"). In this case, a measuring-plane product of a sample is a 1micrometerx1micrometer square, and is the number of point of measurement. The shape of surface type was measured in 512x256 points, scan speed of 1.02Hz, and DFM (cyclic contact mode), amendment by low pass filter and leveling amendment (with the least square approximation, an inclination of data is amended, and distortion of Z shaft orientations is removed further) of measurement data were performed, and surface roughness Ra and Sm value were computed. [in quest of a curved surface] An electron microscope (for example, Hitachi Make H-600) other than an atomic force microscope is calculable from a profile curve used and measured [observed and].

[0016] When a film which has a refractive index (n) and thickness (d) of a glass base material smaller than a refractive index on the surface of a glass substrate is covered, conditions from which a reflection factor in the incident angle alpha becomes min make lambda wavelength of light, and m is expressed with the following formula 1 as zero or a positive integer.

[Equation 1]

$$2=\lambda [d(n^2-\sin^2\alpha)] / (1+2m)/4 \quad (1)$$

[0017] The thickness (d) from which the light reflection factor of a high incident angle, for example, the incident angle of 60 degrees, becomes min is expressed with the following formula 2 which substitutes alpha= 60 and m= 0 for the above-mentioned formula 1, and is obtained. In a formula 2, in the wavelength lambda of 380-780nm either of the light regions, the film of a refractive index n can make the reflection factor of the light of the wavelength min, if the thickness (d) of the following type is satisfied. In addition, if m is made into 1 or 2 or more, since thickness will become very large and absorption of the light will become large, it is not desirable. Since the refractive indexes of the film which consists of the chain-like silica particle and silica in this invention are 1.25-1.40 as mentioned above, the thickness from which a light reflection factor serves as min is set to 86-216nm from the above-mentioned formula 2. However, the thickness in this invention defines it as the height from a glass plate front face to the heights summit of the film which has surface irregularity. Therefore, since, as for the thickness of this definition, only the arithmetic mean granularity (Ra) and this degree on the front face of a film become large as compared with the thickness of the above-mentioned formula 2, as for the thickness in this invention, it is desirable actually that it is 110-250nm.

[Equation 2]

$$d=(\lambda/4) \times (n^2-3/4)-1/2 \quad (2)$$

[0018] The film which consists of a chain-like silica particle and a silica is formed in the one side front face or both the front faces of a glass substrate. When a refractive index [like air and a gas] both whose front faces of a glass plate are is faced and used for data medium near 1, the acid-resisting [make / to form this film in both the front faces of a glass substrate / higher] effect is acquired. However, when a front face is faced and used for data medium near the refractive index of a glass substrate of a glass substrate on the other hand, for example, when the glass plate of two sheets is joined through a transparence resin layer like a polyvinyl butyral between them Since the light echo by the interface of a glass plate and a transparence resin layer can be disregarded, it is enough as the film which consists of a chain-like silica particle and a silica for the glass plate front face facing a transparence resin layer just to make it form only in the outside front face of each glass plate, without making it form.

[0019] A chain-like silica particle is preferably used in the form of a solvent distribution sol. As an example of a chain-like silica particle sol, "Snow tex-OUP" by Nissan Chemical Industries, Ltd. and

"Snow tex-UP" are mentioned, for example. These have the average diameter of 10-20nm, and an average length of 60-200nm, and have the configuration which curved in three dimensions.

[0020] Although the solvent of the above-mentioned particle will not be especially limited if the particle is distributing to stability substantially, its simple substance or mixtures, such as water, a methanol, ethanol, propanol, ethylcellosolve, butyl cellosolve, and propyl cellosolve, are desirable, and water and its propyl cellosolve are still more desirable. Since these water and lower alcohol are simply mixed with the solution containing the above-mentioned organometallic compound and heat treatment after membrane formation can remove them easily, they are good. Among these, water and propyl cellosolve are the most desirable on manufacture environment.

[0021] In this invention, the coat of a silica film which has the surface irregularity to a glass substrate applies and forms the liquid containing at least one sort of silicon compounds chosen from the group which serves as for example, a chain-like silica particle from the organosilicon compound in which hydrolysis and condensation polymerization are possible, chlorosilyl radical content silicon compounds, and those hydrolyzates on a glass substrate.

[0022] A distributed assistant may be added in case the above-mentioned particle is added in the solution containing the organosilicon compound in which the above-mentioned hydrolysis and condensation polymerization are possible, and a chlorosilyl radical content silicon compound. Especially a distributed assistant is not limited, but electrolytes, such as the additive generally used, for example, sodium phosphate, hexametaphosphoric acid sodium, a potassium pyrophosphate, an aluminum chloride, and ferric chloride, various surfactants, various organic macromolecules, a silane coupling agent, a titanium coupling agent, etc. are used, and the addition is usually 0.01 - 5 % of the weight to the above-mentioned colloid or a particle.

[0023] Although what kind of compound is fundamentally sufficient as it as long as the organosilicon compound which is included in liquid with the above-mentioned silica particle and in which hydrolysis and condensation polymerization are possible performs hydrolysis and dehydration condensation, the alkoxide of silicon and its chelate of silicon are desirable.

[0024] As a silicon alkoxide, the methoxide of silicon, ethoxide, propoxide, butoxide, etc. are preferably used as a simple substance or a mixture, and, specifically, the acetylacetonate complex of silicon is preferably used as a silicon chelate.

[0025] Moreover, alkyl silicate 40, for example, the "ethyl silicate" by COL coat incorporated company, and "MS56" by Mitsubishi Chemical, Inc. etc. can be used as the above-mentioned organosilicon compound. [amount of macromolecules type]

[0026] As the above-mentioned organosilicon compound hydrolyzate, made in a commercial alcoxysilane hydrolysis liquid, for example, "HAS-10", Inc. by COL coat incorporated company Japanese, board lab "Serra Mika G-91", "G-92-6", and "ATORON NSI-500" by Nippon Soda Co., Ltd. etc. can be used.

[0027] With the chlorosilyl radical content compound included in liquid with the above-mentioned chain-like silica particle Chlorosilyl radical (n is 1, 2, or 3 in $-\text{SiCl}_n\text{X}_{3-n}$ and here) X -- hydrogen -- or -- respectively -- a carbon number -- the alkyl group of 1-10, and an alkoxy group -- It is the compound which it has at least one piece in intramolecular. or an acyloxy radical -- it is -- Also in it, the compound which has at least two chlorine is desirable, and chlorine replaces at least two hydrogen in silane SiH_{2n+2} (n is the integer of 1-5 here). The chlorosilane which replaced other hydrogen by the above-mentioned alkyl group, the alkoxy group, or the acyloxy radical if needed, and its condensation polymerization object are desirable. For example, tetra-chlorosilane (a silicon tetrachloride, SiCl_4), trichlorosilane (SiHCl_3), A TORIKURORO monomethyl silane (SiCH_3Cl_3), dichlorosilane (SiH_2Cl_2), $\text{Cl}-(\text{SiCl}_2\text{O})_n-\text{SiCl}_3$ (n is the integer of 1-10), etc. can be mentioned. Although the hydrolyzate of the above-mentioned chlorosilyl radical content compound can also be used, and it is independent or can be used combining plurality out of these, the most desirable chlorosilyl radical content compound is tetra-chlorosilane. A chlorosilyl radical has dramatically high reactivity and by carrying out self-condensation or a substrate front face, and a condensation reaction shows firm adhesive strength.

[0028] The above-mentioned chain-like silica particle is distributed, and although the solvent of the

solution containing the above-mentioned organosilicon compound, chlorosilyl radical content compounds, or those hydrolyzates is fundamentally good anything if the above-mentioned organosilicon compound or its hydrolyzate is dissolved substantially, alcohols, such as a methanol, ethanol, propanol, and a butanol, ethylcellosolve, butyl cellosolve, and its propyl cellosolve are the most desirable. Although the amount of the chain-like silica particle to distribute is also related, since it becomes impossible to produce opening sufficient between the above-mentioned particles in a film if the concentration of the above-mentioned organosilicon compound dissolved in the above-mentioned solvent is too high not much, it is desirable to consider as 20 or less % of the weight, and 1 - 20% of the weight of concentration is desirable. And the amount (sum total) of the above-mentioned organosilicon compound to the amount of the chain-like silica particle in a solution, chlorosilyl radical content compounds, or those hydrolyzates is silica conversion, and its 5 - 30 % of the weight is desirable to 100 % of the weight of chain-like silica particles.

[0029] Water is required for hydrolysis of the above-mentioned organosilicon compound. Although acidity and neutral any are sufficient as this, in order to promote hydrolysis, it is desirable to use the water made into acidity with a hydrochloric acid, a nitric acid, the sulfuric acid, the acetic acid, the citric acid, the sulfonic acid, etc. Although especially the addition of an acid is not limited, 0.001-2 are good to an organosilicon compound at a mole ratio. If there is less addition acidity at a mole ratio than 0.001, even if acceleration of hydrolysis of an organosilicon compound is not enough and there is at a mole ratio than 2, the effect of acceleration of hydrolysis does not improve any longer, and it is not desirable.

[more]

[0030] As for the addition of water required for hydrolysis of the above-mentioned organosilicon compound, 0.1-100 are good to an organosilicon compound at a mole ratio. If there are few water additions at a mole ratio than 0.1, acceleration of hydrolysis of an organosilicon compound is not enough, and it becomes the inclination for the stability of liquid to fall and is not desirable if [than 100] more [in a mole ratio].

[0031] To use the above-mentioned chlorosilyl radical content compound, neither water nor an acid necessarily needs to be added. Even if it adds neither water nor an acid at all additionally, hydrolysis advances with the moisture contained in the solvent, the moisture in an ambient atmosphere, etc. Moreover, a hydrochloric acid separates in liquid with this hydrolysis, and hydrolysis advances further. However, even if it adds water and an acid additionally, it does not interfere at all.

[0032] The above-mentioned organosilicon compound, chlorosilyl radical content compounds, or those hydrolyzates are mixed with the above-mentioned chain-like silica particle with a solvent, water, an acid catalyst, and a distributed assistant are added if needed, and the coating liquid for forming irregularity on a substrate is prepared. At this time, an organometallic compound and a chlorosilyl radical content compound may be used independently, or it may mix, and they may be used, or whichever is sufficient as them. The desirable raw material compounding ratio of this coating liquid is as in the following table 1. The silicon compound expresses the above-mentioned organosilicon compound, chlorosilyl radical content compounds, or those hydrolyzates in the sum total here.

[0033]

[A table 1]

===== silicon compound 100 weight ****-like silica particle 100 - 800 weight
 **** 4 - 150 weight section acid catalyst 0.00001 - 5 weight partial powder assistant 0.001 - 10 weight
 section solvent 500 - 10000 weight section ===== [0034] The above-mentioned organometallic compound or a chlorosilyl radical content compound is melted to a solvent, a catalyst and water are added, and it hydrolyzes for two days from for 5 minutes at a predetermined temperature during the boiling point of 10 degrees C and a solution. Add a distributed assistant there a chain-like silica particle and if needed, it is made to react for two days from for 5 minutes if needed at a predetermined temperature during the boiling point of 10 more degrees C and a solution, and coating liquid is obtained. In addition, when using a chlorosilyl radical content compound, it is not necessary to add a catalyst and water specially. Moreover, a chain-like silica particle may be added before the above-mentioned hydrolysis process. Moreover, in order to skip the hydrolysis process of an organosilicon

compound, the organometallic compound hydrolyzate solution of the above-mentioned marketing may be used. The obtained coating liquid may be diluted with a suitable solvent according to the coating method after that.

[0035] The above-mentioned coating liquid is applied on a glass substrate, it dries and a silica irregularity film is formed on a glass substrate.

[0036] Although the method of the above-mentioned spreading is not limited that what is necessary is just to especially use well-known technology, various print processes, such as methods, such as a method using equipments, such as a spin coater, a roll coater, a spray coater, and a curtain coating machine, and the immersion Czochralski method (DIP coating method), a flow-coating method (the flow coating method), and screen-stencil, gravure, curved surface printing, are used.

[0037] Although the above-mentioned coating liquid may be crawled depending on a glass substrate and it may be unable to apply to homogeneity, it can be improved by this by performing washing and surface treatment on the front face of a substrate. As the method of washing or surface treatment, degreasing washing by organic solvents, such as alcohol, an acetone, and a hexane, washing by alkali or the acid, the method of grinding a front face by the abrasive material, ultrasonic cleaning, UV irradiation processing, ultraviolet-rays ozonization, plasma treatment, etc. are mentioned.

[0038] A silica irregularity film is formed by drying the glass substrate after spreading from for 1 minute at the temperature between 200 degrees C from a room temperature for 2 hours. If it heat-treats from 5 seconds at the temperature between 400 degrees C - 750 degrees C after that for 5 hours if needed, thereby, the silica irregularity film on the front face of a glass substrate will become firm. This concavo-convex film consists of a matrix of a chain-like silica particle and a silica (it originates in an organometallic compound), a chain-like silica particle fixes to a glass substrate by the silica matrix, and the shape of surface type of a chain-like silica particle forms the irregularity of this film.

[0039] As a glass substrate before [above] spreading is carried out, glass plates, such as a windshield for automobiles which finished the bending process and the doubling process, a rear window, a front door, or a rear door, may be used, it may be before the bending process in front of a doubling process, or you may be the glass plate before being cut by the predetermined size.

[0040] The glass plate for automobiles which covered the silica irregularity film can cover a water-repellent coat or a fog resistance coat on the front face further. When the water-repellent engine performance is obtained and dirt adheres by covering a water-repellent coat, dirt clearance nature can also be improved. Moreover, when fog resistance ability is obtained and dirt adheres by covering an antifog aquosity coat, dirt clearance nature can also be improved. A silica irregularity film may be covered on both the front faces of a glass plate (a glass laminate board may be used), a water-repellent coat may be covered on the front face of one of these, or both front faces, a silica irregularity film may be covered on the single-sided front face of a glass plate, and a water-repellent coat may be covered on either both a silica irregularity film and a bare glass front face. Even if the water-repellent coat is covered on the silica irregularity film, light acid resistibility ability and visibility do not fall.

[0041] A silica irregularity film may be similarly covered on both the front faces of a glass plate (a glass laminate board may be used), a fog resistance coat may be covered on the front face of one [at least] of these, a silica irregularity film may be covered on the single-sided front face of a glass plate (a glass laminate board may be used), and a fog resistance coat may be covered on [the] either both a silica irregularity film and a bare glass front face.

[0042] Moreover, when this invention is applied to the aperture for automobiles, it is desirable that a silica irregularity film is covered by the both-sides front face of a glass plate (a glass laminate board may be used), a fog resistance coat is covered by the front face (vehicle inside) of said film of one side, and the water-repellent coat is covered by said layer membrane side (vehicle outside) of the other side.

[0043]

[Embodiment of the Invention] This invention is not limited by these although the example of this invention is given and explained below.

[0044] The hydrolysis condensation polymerization liquid (trade name: HAS-10, COL coat incorporated company make, and SiO₂ 10 % of the weight of contents) 3.0 weight section of [example 1] ethyl

silicate, The chain-like silica colloid (trade name: Snow tex OUP, Nissan Chemical Industries, Ltd. make, 15 % of the weight [of solid content], distributed assistant content) 13.3 weight section whose average length an average diameter is about 170nm in about 15nm, 2-propanol The 74.9 weight sections were mixed at the room temperature, this was diluted with 2-propanol 3 weight twice, it stirred at the room temperature for 2 hours, and the coating liquid for low refractive-index irregularity stratification was obtained. In this coating liquid, a chain-like silica particle and ethyl silicate contained by the weight ratio of 100:15 by silica conversion, respectively. Moreover, to the silicon compound 100 weight section, the 670 weight sections and moisture were contained for the chain-like silica particle, and, as for it, this coating liquid contained the 4.5 weight sections and a solvent for 45 weight sections and an acid catalyst, respectively.

[0045] Coating liquid was applied on both the front faces of a glass plate by front-face-grinding, washing by the cerium oxide system abrasive material, being immersed in said coating liquid for low refractive-index irregularity stratification, and pulling up the soda lime silicate glass board (65mmx150mmx3mm) which performed ultrasonic cleaning and was dried the speed for 20cm/in pure water, further. After drying this glass plate for 30 minutes at 100 degrees C and making it dry for 30 minutes at 250 more degrees C, it heat-treated within 500-degree-C oven for 1 hour, and the glass plate with which the silica irregularity film with a thickness of 140nm was formed in each front face was obtained. In addition, 140nm of this thickness is almost equal to the value of 134nm to which thickness calculated the above-mentioned formula 2 to light with a wavelength (λ) of 550nm as (refractive-index n) = 1.340 of the conditions from which a reflection factor serves as min, i.e., a film, when an incident angle (α) is 60 degrees.

[0046] The thickness of a silica irregularity film, a membranous refractive index, film voidage, film surface roughness, the light reflection factor of a glass plate with a silica irregularity film, and measurement of visibility were performed as follows.

Thickness of a silica irregularity film; the cross section of the glass plate with which the silica irregularity film was covered was observed by one 100,000 times the scale factor of this with the electron microscope, and the height from a glass plate front face to the heights summit of a concavo-convex film was made into thickness.

A membranous refractive index; the value in light with a wavelength of 550nm is calculated by the ellipsometer.

Film voidage; the magnitude of an opening is measured and calculated from an electron microscope photograph.

[0047] Film surface roughness; from the profile curve which observed and measured the film using the atomic force microscope (SPI3700 by SEIKO electronic incorporated company) Arithmetic mean granularity (Ra value) and a concavo-convex average gap (Sm value) are JIS. B The value defined by the method given in 0601 (1994) was calculated.

[0048] Light reflection factor; the reflected light from both sides of a glass plate was measured for the reflection factor of the incident angle of 12 degrees, and the light (380-780nm wavelength) in 60 degrees using the spectrophotometer (MCPD-1000, Otsuka electronic incorporated company make).

[0049] Visibility: When other one side (left half) attached a non-processed glass plate for a glass plate with a silica irregularity film, respectively and the outside of a vehicle inside empty vehicle was seen in one side (right half) of the windshield of an automobile, it is comparing the glass plate of right and left of the conspicuousness of front scenery, i.e., the degree of the field-of-view active jamming by reflect lump of an instrument panel, and organic-functions assessment was carried out. The criterion was performed on the criteria shown in the following table 2 in 1-5 steps. Those measurement results are shown in a table 3.

[0050]

[A table 2]

===== Visibility organic-functions error-criterion mark
Criteria ----- 1:instrument panel reflect lump is worrisome, and front scenery is hard to see.

- 2: Although instrument panel a reflect lump is worrisome for a while, when it sees carefully, front scenery is in sight. 3: Front scenery looks easily although there is instrument panel a little reflect lump. 4: There is almost no instrument panel reflect lump, and front scenery looks almost clearly. 5: There is no instrument panel reflect lump, and front scenery looks clear.

===== [0051] Instead of the chain-like silica colloid 13.3 weight section of the coating liquid used in the [example 1 of comparison] example 1 silica colloid (trade name: -- the Snow tex OL --) with a particle size of 50nm The Nissan Chemical Industries, Ltd. make, coating liquid which used the 10.0 20 % of the weight weight sections of solid content (a silica particle and ethyl silicate) The dip painting cloth and the glass plate with which it dried, heat-treated and the silica irregularity film with a thickness of 118nm was formed in each front face were obtained on both the front faces of a glass plate like the example 1 using content by the weight ratio of 100:15 by silica conversion, respectively. In addition, 118nm of this thickness of the conditions from which optical thickness is set to $4/\lambda$ to light with a wavelength $[\lambda]$ of 550nm as (refractive-index n) = 1.454 of the conditions and film with which a reflection factor serves as min when an incident angle (α) is 60 degrees, i.e., thickness, is equal to the value of 118nm which calculated the above-mentioned formula 2. The thickness of the obtained silica irregularity film, a membranous refractive index, film voidage, film surface roughness, the light reflection factor of a glass plate with a silica irregularity film, and the measurement result of visibility are shown in a table 3.

[0052] The amount-used 3.0 weight section of the hydrolysis condensation polymerization liquid of the ethyl silicate of the coating liquid used in the [examples 2 and 3 of comparison] example 1 is made into 20 weight sections. Made the chain-like silica particle and ethyl silicate in coating liquid into the weight ratio of 50:50 by silica conversion, respectively, and also The dip painting cloth and the glass plate with which it dried, heat-treated and the silica irregularity film with a thickness of 120nm was formed in each front face were obtained on both the front faces of a glass plate like the example 1 (example 2 of a comparison). In addition, 120nm of this thickness of the conditions from which optical thickness is set to $4/\lambda$ to light with a wavelength $[\lambda]$ of 550nm as (refractive-index n) = 1.432 of the conditions and film with which a reflection factor serves as min when an incident angle (α) is 60 degrees, i.e., thickness, is almost equal to the value of 121nm which calculated the above-mentioned formula 2.

[0053] Moreover, the amount of the chain-like silica colloid used in coating liquid was made into zero, and also like the example 1, on both the front faces of a glass plate, it dried and heat-treated and the silica film with a thickness of 115nm obtained the dip painting cloth and the glass plate formed in each front face (example 3 of a comparison). In addition, 115nm of this thickness is equal to the value of 115nm to which thickness calculated the above-mentioned formula 2 to light with a wavelength $[\lambda]$ of 550nm as (refractive-index n) = 1.473 of the conditions and film with which a reflection factor serves as min when an incident angle (α) is 60 degrees. The thickness of the obtained silica irregularity film, a membranous refractive index, film voidage, film surface roughness, the light reflection factor of a glass plate with a silica irregularity film, and the measurement result of visibility are shown in a table 3. In addition, the unsettled visible-ray reflection factors of the 12 degrees and the 60-degree incident angle of a glass plate (refractive index 1.5) are about 7% and about 14%, respectively.

[0054]

[A table 3]

===== ** Surface roughness Light reflection factor (%) **
 Thickness Chip box Voidage (nm) ----- A private seal (nm) Rate (volume %) ----- incident angle
 Incident angle A sex Ra Sm 12 degrees 60 degrees ----- Example 1 1401.340 60
 720 0.81.9 Example 1 of 5 comparisons 118 1.454 156 20 1.8 Example of 4.3 4 comparison 2 120 1.432
 2 5 - 4 8 Example 3 of 3 comparisons 115 1.47300 - 8 14.5

1===== [0055] Instead of the soda lime silicate glass board (65mmx150mmx3mm) used in the [example 2] above-mentioned example 1 The glass plate for automobile windshields (about 150cmx about 60cmx 3mm) which has the same soda lime silicate glass

presentation is used. Like the example 1, a dip painting cloth and after drying, it heat-treated according to the well-known bending process (it heats for 15 minutes at 570 degrees C), and the glass plate for automobile windshields with which the silica irregularity film with a thickness of 120nm was formed in each front face was manufactured.

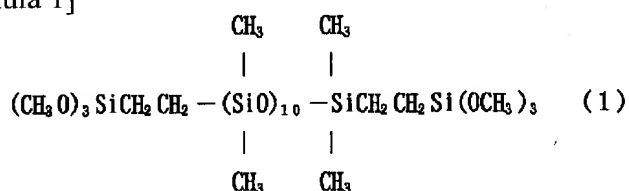
[0056] About this glass plate, when the thickness of a concavo-convex film, a membranous refractive index, film voidage, film surface roughness, a light reflection factor, and visibility were measured, the same result as an example 1 was obtained. And about membranous reinforcement, after performing 100 round-trip grinding, applying the load of 500gf(s) using the cheesecloth which attached the commercial glass cleaner, the film was observed with the naked eye, and the existence of abnormalities was investigated, and this was counted with 1 time and it examined repeatedly. Although 300 times of grinding showed abnormalities in the example 1, an example 2 did not show abnormalities to 5000 times of grinding.

[0057] The two above-mentioned glass plates for automobile windshields with a silica irregularity film were prepared, the well-known doubling process was passed, and the glass laminate board for automobile windshields joined through the polyvinyl-butyril interlayer whose thickness is 0.7mm was obtained. This glass laminate board showed a light reflection factor almost equal to an example 1, and visibility.

[0058] To the 1l. glass reactor equipped with the [example 3] thermometer, the agitator, and the condensator Formula C8F17CH2CH2Si3 (OCH3) 10.0g of perphloro radical content organosilicon compounds shown, 10.0g of hydrolysis nature machine content methyopolysiloxane compounds shown with the following chemical formula 1, 1.94g of t-butanols [360.0g and 0.1N] hydrochloric-acid aqueous solutions was prepared, the cohydrolysis reaction was carried out at 80 degrees C for 5 hours, n-hexane 160.0g which is a hydrophobic solvent was added further, and it agitated at the room temperature for 10 hours.

[0059]

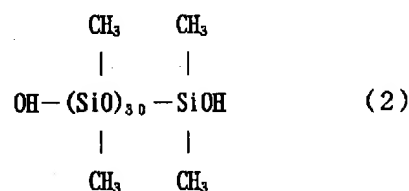
[Formula 1]



[0060] Subsequently, organopolysiloxane 10.0g shown in this with the following chemical formula 2 and 5.0g of methansulfonic acid were added, it agitated for 10 minutes, and the constituent for water-repellent film formation was obtained.

[0061]

[Formula 2]



[0062] After having applied the 0.1ml of the above-mentioned constituents for water-repellent film formation 10 times, lengthening them with the cheesecloth on the front face of one concavo-convex layer of the silica irregularity layer coat glass plate obtained in said example 1 and wiping off excessive spreading liquid with a dry towel, it heat-treated for 10 minutes at 100 degrees C, and the low reflective water repellence glass plate which has the water-repellent film whose thickness is 40nm was obtained. Moreover, appearance quality was good, although the water-repellent film was observed with the naked eye and the existence of abnormalities was investigated.

[0063] Using the contact angle meter ("CA-DT" by consonance interface science incorporated company), the contact angle with the water of the obtained water-repellent film measured the contact angle of waterdrop with a diameter of about 2mm, and carried out abrasion resistance, chemical resistance, and a weathering test. It was shown that water repellence is excellent so that the contact angle was high, but although the contact angle after a weathering test was low as a result was shown in a table 4, each of initial-contact angles, contact angles after an abrasion resistant test, and contact angles after a chemical corrosion resistance test is 95 degrees or more, and was dramatically excellent. And when incidence of the light was carried out to that water-repellent film surface from the reverse front face, the light reflection factor was measured, and the water-repellent film surface was made into the vehicle outside and visibility was measured about this low reflective water repellence glass plate, as for each of initial value, values after an abrasion resistant test, and values after a chemical corrosion resistance test, the result completely equivalent to an example 1 was obtained.

[0064] In addition, an abrasion resistant test attaches a dry towel in the both-way abrasion tester made from new east science, and is 0.3kg/cm² of loads here. By measuring the contact angle after carrying out 3000 ****s of water-repellent film front faces A chemical corrosion resistance test by measuring the contact angle after being immersed in the saturated lime water solution for 24 hours weatherability On the conditions of an every 30-second room shower ring the whole hour using a weather meter "the eye super UV circuit tester W13" (Iwasaki Electric make) illuminance 76**2 mW/m² and the black panel temperature of 48**2 degrees C By measuring the contact angle after 400-hour UV irradiation, it carried out, respectively.

[0065]

[A table 4]

===== A water-repellent film The first stage ----- contact
angle Abrasion resistance Chemical resistance Weatherability thickness (nm) Appearance quality
(degree) (Degree) (Degree) (Degree) ----- Example 3 40 Good 107 100 101
85===== [0066] [Example 4] 1ml added to 1000ml

commercial ethanol (99.5%), and 0.1-N acetic acid was stirred to it. 4g ("SIM 6492.7" by Chisso Corp., 90% of content, molecular weight 460-590, ethyleneoxide units 6-9) of [methoxy (polyethyleneoxy) propyl] trimethoxysilane was added in 796g of liquid which makes this ethanol a subject, it stirred at 30 degrees C for 1 hour, and organosilane spreading liquid was prepared.

[0067] Liquid was applied on both the front faces of a glass plate with a silica irregularity film by being immersed in the above-mentioned organosilane spreading liquid; and pulling up the silica irregularity layer coat glass plate obtained in said example 1 the speed for 5cm/, after cleaning ultrasonically and drying in pure water. After drying and heat-treating this glass plate for 30 minutes and cooling it to a room temperature at 120 degrees C, pure water washed lightly, and the glass plate with a fog resistance silica irregularity film with which the organosilane layer which contains a polyethylene oxide radical in intramolecular, and whose thickness is about 8nm was formed was obtained.

[0068] When incidence of the light was carried out, and the light reflection factor was measured and visibility was measured about this low reflective fog resistance glass plate, the result completely equivalent to an example 1 was obtained. Moreover, surface roughness measurement, contact angle measurement, first stage, and repeat fog resistance assessment was performed by the method shown below about this glass plate with a fog resistance silica irregularity film. As for these measurement results, it turned out that it has the fog resistance ability which was excellent as shown in a table 5, and dirt cannot adsorb easily and it has good antifog maintenance nature and antifouling property ability.

[0069]

[A table 5]

===== Surface roughness The first Term Repeat fog resistance
(nm) ----- sample ----- contact angle It blooms cloudy. Distortion Cloudiness Distortion Ra
Sm (degree) Assessment Assessment Assessment Assessment ----- Example 4 6
20 3 0 0 4 5===== [0070] It asked for arithmetic mean
granularity (Ra) and a concavo-convex average gap (Sm) by the same method as the measurement about

the silica irregularity film of an example 1 about the glass plate with which surface roughness and the contact angle measurement above-mentioned organosilane coat silica irregularity film were formed. Moreover, the contact angle over 0.4mg waterdrop was measured using the contact angle meter ("CA-DT" by consonance interface science incorporated company). It is shown that fog resistance is excellent, so that the value of a contact angle is small.

[0071] The glass plate with which the fog resistance assessment above-mentioned fog resistance silica irregularity film was formed The temperature of 5 degrees C, the constant temperature of 10% of relative humidity -- the temperature of 25 degrees C, after placing into a constant humidity chamber and putting for 10 minutes the constant temperature of 70% of relative humidity -- it moved in the constant humidity chamber, it observed with both the degree of cloudiness until 2 minutes pass since the time of 30 seconds passing, and the degree [image / after 2 minute progress / fluoroscopy] of distortion, the minute waterdrop adhesion condition of the front face of a glass plate was investigated, and four-step assessment shown in a table 6 was performed.

[0072]

[A table 6]

=====	
曇り評価	曇り状態

◎	全く曇らない
○	薄く曇る
△	ゆっくりだが濃く曇る
×	すぐ濃く曇る
=====	
透視歪み評価	透視像歪み状態

◎	全く歪まない
○	少し歪む
△	かなり歪む
×	激しく歪む
=====	

[0073] Repetition fog resistance assessment JIS S The above-mentioned sample board was installed in the cooling system (product made of a transparent plastic) given in 4030-1995 "the cloudy stop agent test method for glasses", the sample rear face was contacted to cooling water, and sample temperature was kept at 20 degrees C. having cooled the sample in this condition -- the constant temperature of the temperature of 45 degrees C, and 80% of relative humidity RH -- it placed into the constant humidity chamber and maintained for 3 minutes. then, having stuck the sample to the cooling system -- this -- the constant temperature of the temperature of 20 degrees C, and 10% of relative humidity RH -- it placed into the constant humidity chamber and was made to dry for 3 minutes Actuation of this high humidity ambient atmosphere exposure and low humidity ambient atmosphere exposure was made into 1 cycle, and 30 cycle was repeated.

[0074] The test chart for a fluoroscopy distortion judging printed on the plastic sheet is stuck on the rear face of the above-mentioned cooling system after this repetition actuation, water is infiltrated into the crevice on a board and the rear face of a cooling system, and it enabled it to observe the test chart for a fluoroscopy distortion judging from a sample side. The test chart for a fluoroscopy distortion judging is JIS. S The test chart of attached chart 1 publication of 4030-1995 was imitated, the length of three white lines was set to 10mm, and the line breadth and gap were made into five steps, 0.15mm, 0.5mm, 1.0mm, 1.5mm, and 2.0mm. the circulating water temperature of the cooling system which has attached the sample -- 5 degrees C -- lowering and this -- the constant temperature of the temperature of 25 degrees

C, and 80% of relative humidity RH -- it placed into the constant humidity chamber, the generating condition of cloudiness and fluoroscopy distortion was investigated using the above-mentioned test chart for a fluoroscopy distortion judging, and six-step assessment was performed on the criteria shown in a table 7.

[0075]

[A table 7]

===== cloudiness assessment A cloudy condition -----
 ----- 5 The whole surface does not bloom cloudy mostly. 4 80% or more of area does not bloom cloudy. 3 60% or more of area does not bloom cloudy. 2 60% or more of area blooms cloudy. 1 80% or more of area blooms cloudy. 0 The whole surface blooms cloudy mostly. =

===== fluoroscopy distortion assessment A fluoroscopy distortion condition ----- 5 -- it is not distorted at all -- 3 which separates the white line of a 4 0.15mm gap, and is hard to accept A white line with a gap of 0.5mm or less is separated, and it is hard to accept. 2 A white line with a gap of 1.0mm or less is separated, and it is hard to accept. 1 A white line with a gap of 1.5mm or less is separated, and it is hard to accept. 0

===== which separates a white line with a gap of 2.0mm or less, and is hard to accept [0076] The silica irregularity film with a thickness of 120nm obtained in the [example 5] example 2 sandwiched the polyvinyl-butyl film whose thickness is about 0.5mm in the meantime about two glass plates for automobile windshields formed in each front face, vacuum pressure arrival was carried out at about 140-150 degrees C in the autoclave, and the glass laminate board was obtained. After drying and heat-treating for 30 minutes and cooling to a room temperature at 120 degrees C after carrying out gravure coating of the viscous regulator to the organosilane spreading liquid used for the vehicle inside front face of this glass laminate board in the example 4 using the liquid which carried out optimum dose addition, pure water washed lightly, and the organosilane antifog layer which contains a polyethylene oxide radical in intramolecular and whose thickness is about 8nm was covered inside.

[0077] Next, after having applied 10 times, lengthening with the cheesecloth which made 1.0ml of constituents for water-repellent film formation prepared in the example 3 adhere to the vehicle outside front face of this glass plate and wiping off excessive spreading liquid with a dry towel, it heat-treated for 10 minutes at 100 degrees C, and low reflective water repellence was given to the vehicle outside front face.

[0078] Thereby, the glass plate for automobile windshields by which the laminating was carried out to the order of a water-repellent coat-silica irregularity film-glass plate-silica irregularity film-polyvinyl-butyl film-silica irregularity film-glass plate-silica irregularity film-anti-fogging film was obtained seen from the vehicle outside.

[0079] When the fog resistance ability of the vehicle inside front face of this glass plate and the water-repellent engine performance of a vehicle outside front face were measured, it turned out that it has good fog resistance ability equivalent to the measurement result of an example 4, and the good water-repellent engine performance equivalent to the measurement result of an example 3. And when incidence of the light was carried out from that anti-fogging film side, the light reflection factor was measured, and the water-repellent film surface was made into the vehicle outside and visibility was measured about this glass plate, the result with both a light reflection factor and visibility completely equivalent to an example 1 was obtained.

[0080] In addition, since the refractive index of the above-mentioned polyvinyl-butyl film was almost equal to it of a glass plate, even if it prepared the silica irregularity film inside a glass plate (side carried out in contact with the polyvinyl-butyl film) and had not prepared it, acid resistibility ability hardly changed it.

[0081] Coating liquid was prepared like the example 1 except having changed the compounding ratio of the hydrolysis condensation polymerization liquid of the ethyl silicate used for preparation of the coating liquid in the [examples 6 and 7] example 1, chain-like silica colloid (trade name: Snow tex OUP), and 2-propanol, as shown in a table 8. In this coating liquid, a chain-like silica particle and ethyl

silicate contained by the weight ratio shown in a table 8 by silica conversion, respectively.

[0082] Next, this coating liquid was used, it applied, dried and heat-treated on the same conditions as an example 1 to the same glass plate as an example 1, and the glass plate with which the silica irregularity film was formed in both front faces was obtained. The result of having measured the thickness of the obtained silica irregularity film, a membranous refractive index, film voidage, film surface roughness, the light reflection factor of a glass plate with a silica irregularity film, and visibility like the example 1 is shown in a table 9.

[0083]

[A table 8]

===== Ethyl silicate Hydrolysis Chain-like silica 2-pro
Condensation polymerization liquid Colloid PANORU Chain-like particle: Ethyl silicate (weight
section) (weight section) (weight section) (silica equivalent weight ratio)

----- Example 1 3.0 13.3 74.9 100:15 examples 6 1.4 13.3 74.9 100:7 examples 7
5.0 13.3 74.9 100:25===== [0084]

[A table 9]

===== ** Surface roughness Light reflection factor (%) **
Thickness Chip box Voidage (nm) ----- A private seal (nm) Rate (volume %) ----- incident angle
Incident angle A sex Ra Sm 12 degrees 60 degrees ----- example 6 115 1.28 70
10 22 0.7 1.9 5 Example 7 1601.38 55 7 20 2.2 3.2 5 =====

[0085]

[Effect of the Invention] Since the layer which has surface irregularity and a low refractive index in a glass plate is covered according to this invention, the glass plate suitable for the light reflection factor of a glass plate and the aperture for the automobiles which have the outstanding visibility since especially the light reflection factor in the high incident angle of 60 degrees becomes small with 4.0% or less (when it covers to both sides of a glass plate) and the anti-dazzle effect is moreover acquired with surface irregularity is obtained.

[Translation done.]

* NOTICES *

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2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] A light acid-resisting glass plate with which it consists of 5 - 30% of the weight of a silica to weight of a chain-like silica particle and its chain-like silica particle, a film which has thickness of 110-250nm is covered by at least one side on a front face of a glass substrate, and irregularity is formed in the film front face.

[Claim 2] An acid-resisting glass plate with which it consists of a chain-like silica particle and a silica, and a film which has thickness of 110-250nm is covered by at least one side on a front face of a glass substrate, an opening is generated, the film has a refractive index of 1.25-1.40 between chain-like silica particles which adjoin mutually within a film, and irregularity is formed in the film front face.

[Claim 3] Said chain-like silica particle is an acid-resisting glass plate according to claim 1 or 2 which has an average diameter of 10-20nm, and an average length of 60-200nm.

[Claim 4] Irregularity on said front face of a film is an acid-resisting glass plate given in any 1 term of claims 1-3 which have 5-50nm arithmetic mean granularity (Ra) and an average gap (Sm) with an irregularity of 10-300nm.

[Claim 5] An acid-resisting glass plate given in any 1 term of claims 1-4 with which a water-repellent coat is further covered by front face of said glass substrate with which a front face of said film and/or said film are not covered.

[Claim 6] An acid-resisting glass plate given in any 1 term of claims 1-4 with which a fog resistance coat is further covered by front face of said glass substrate with which a front face of said film and/or said film are not covered.

[Claim 7] An acid-resisting glass plate given in any 1 term of claims 1-4 with which said film is covered by front face of both said glass substrates, a fog resistance coat is covered by said one film front face, and a water-repellent coat is covered by said film front face of another side.

[Claim 8] An acid-resisting glass plate given in any 1 term of claims 1-4 of said glass substrate with which said film is covered by only front face on the other hand, a fog resistance coat is covered by front face of said film, and a water-repellent coat is covered by another side front face of said glass substrate.

[Claim 9] (1) A manufacture method of an acid-resisting glass plate characterized by applying and drying liquid containing at least one sort of silicon compounds chosen from a group which serves as a chain-like silica particle from an organosilicon compound in which (2) hydrolysis and condensation polymerization are possible, chlorosilyl radical content silicon compounds, and those hydrolyzates on a glass substrate front face, and forming a silica irregularity film in a glass substrate front face.

[Claim 10] Said liquid is SiO₂ about said chain-like silica particle and said silicon compound, respectively. A manufacture method of an acid-resisting glass plate according to claim 9 which carries out 5-30 weight section content of said silicon compound to said chain-like silica particle 100 weight section by conversion.

[Claim 11] Said liquid is the manufacture method of an acid-resisting glass plate according to claim 9 or 10 which consists of the following combination.

A silicon compound A 100 weight ****-like silica particle 100 - 800 weight **** A 4 - 150 weight

section acid catalyst 0.00001 - 5 weight partial powder assistant 0.001 - 10 weight section solvent The 500 - 10000 weight section [Claim 12] A manufacture method of an acid-resisting glass plate given in any 1 term of claims 9-12 heated at 400-750 degrees C after said spreading / desiccation for 5 seconds to 5 hours.

[Claim 13] A coat constituent for antireflection films which consists of the following combination. A silicon compound A 100 weight ****-like silica particle 100 - 800 weight **** A 4 - 150 weight section acid catalyst 0.00001 - 5 weight partial powder assistant 0.001 - 10 weight section solvent The 500 - 10000 weight section

[Translation done.]